SURFACE MODIFICATION OF Ti-6Al-4V

BY

ELECTROCHEMICAL OXIDATION

A thesis submitted in partial fulfilment of the requirement for the degree of

MASTER of TECHNOLOGY

In

BIO-MEDICAL ENGINEERING

By

CHANDAN KUMAR (211BM1212)

Department of Biotechnology and Medical Engineering

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CERTIFICATE

This is to certify that the thesis entitled '**Surface modification of Ti-6Al-4V by electrochemical oxidation'** submitted by **Chandan kumar (211bm1212)** in partial fulfilment of the requirements for the award of Master of Technology from the Department of Biotechnology and Medical Engineering with specialization in "Biomedical Engineering" at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Place:

Date:

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LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

Ti-6Al-4V:- Titanium-6%Aluminium-4%Vanadium

H.: - hour

V: - Voltage

HF: -Hydroflouric Acid

H_3PO_4:- Phosphoric Acid

H_2SO_4:- Sulphuric Acid

SEM: - Scanning Electron Microscopy

XRD: - X-Ray Diffraction

HVN: - Vicker's Hardness No.

gF :- Ground Force

ml :- milliliters

wt%:- weight percentage

CH_3COOH:- Acetic acid

$CaCl_2$:- Calcium chloride

KCL: - Potassium chloride

$MgCl_2.6H_20$:- Magnesium chloride

$MgSO_4.7H_2O$:- Magnesium Sulphate

NaCl: - Sodium Chloride

$NaHCO_3$:- Sodium hydrogen carbonate

Na_2HPO_4:- Disodium hydrogen Phosphate

$Ti0_2$:- Titanium oxide

CA: - Contact angle

ABSTRACT

Titanium is a metallic biomaterial having multidimensional properties, highly sophisticated function and a wide range of applications in the biomedical field, especially as implants. Titanium is an effective biomaterial for biomedical implants because of its biocompatibility and nontoxicity. Ti-6Al-4V has been used as a substrate in the electrochemical process of anodic oxidation. Two different composition of electrolyte have been chosen for the present study. The first electrolyte consists of CH_3COOH and HF and the second electrolyte consist of H_2SO_4 and HF. Anodic oxidation was carried out in 2-electrode system using a pure graphite rod as the cathode while a polished Titanium sample was used as the anode. The electrochemical oxidation was carried out at a constant voltage supply for different time duration. After deposition, the sample was dried at room temperature for 24 hours and the oxide layer was later analyzed through different characterization techniques. The surface morphology and phase analysis of the coated surface was analyzed by scanning electron microscope (SEM) and X-ray diffraction (XRD). SEM images show the presence of uniformly distributed oxide layer on the Ti-6Al-4V surface. The Micro-hardness test of the electrolytically grown oxide was also carried to determine the hardness of the coating, which confirms that after treatment hardness of Ti-6Al-4V increases with the time duration. Lastly, the wettability test was carried out on the surface of the coated Ti-6Al-4V to evaluate the wetting property of the surface.

Keywords: Ti-6Al-4V, Anodic oxidation, Titanium oxide, wettability.

CONTENTS

3.6 Basic Scheme of Work.

CHAPTER4– RESULTS AND DISCUSSION

4.1 Morphological Characterizations

4.1.1 Scanning Electron Microscopy (SEM) study.

I. Scanning Electron Micrograph of oxide layer deposited in CH_3COOH +0.15 M HF

II. Scanning Electron Micrograph of oxide layer deposited in 1 M H_3SO_4+0.15 % HF

4.2 Phase Analysis by XRD study.

4.3 Micro-Hardness study.

4.4 Wettability study.

CHAPTER5– CONCLUSIONS

References

CHAPTER 1

INTRODUCTION

1.1. INTRODUCTION

Pure titanium and titanium alloys are the most attractive metallic materials for biomedical applications. Ti-6Al-4V has been a main biomedical titanium alloy since a long period. [1]. Biomedical titanium alloys with enhanced biocompatibility have been proposed and are currently under development [2]. These are mainly β type alloys and are composed of non- toxic elements. The β type alloys, also have greater biocompatibility because their moduli are much less than those of α+β type alloys as that of Ti–6Al–4V. These alloys are also able to gain much greater strength and toughness balance. Titanium alloys, especially Ti-6Al-4V are expected to be in much more greater use as implant materials in medical and dental fields due to their superior biocompatibility, corrosion resistance and specific strength compared to other metallic implant materials. [3]. Pure titanium is not as strong as the different alloys of titanium. Maintenance of the long-term stability of implants grafted onto the bone requires good bio-affinity of the biomaterial. Close adhesion with the bone is also mandatory for a prolonged time period [4].

Anodizing is an electrolytic passive process, which is used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is termed anodizing since the metal to be treated forms the anodic electrode of an electrical circuit. Anodizing increases the corrosion resistance as well as wear resistance. Anodic films can also be used for various cosmetic effects with porous coatings quite thick so that they can absorb dyes and also with transparent coatings that can add interference effects to reflected light. Anodic films can be most commonly applied to protect aluminium alloys, although similar processes exist for titanium, zinc, magnesium, niobium, and tantalum. Anodization changes the microscopic surface texture and also changes the metal crystal structure near the surface. Thick coatings are normally porous; therefore a sealing process is usually needed to enhance the corrosion resistance that was previously being obtained. Anodic films are much stronger and much more adherent than most types of paints and metal platings. This makes them less succeptible to crack and peel from aging and wear.

The high affinity of Ti-6Al-4V for oxygen results in several oxides of differing crystalline structures. Natural conditions and a stable atmosphere promote the formation of a thermodynamically stable oxide; i.e. TiO_2, which exists in three crystalline phases which are anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [5]. The anatase structure is usually obtained by anodic oxidation whereas the rutile structure is obtained by anodic oxidation

followed by a heat treatment [6]. The surface morphology and the thickness of the oxide depend mainly on the methods applied for the formation of the oxide layer. The implant-environment interaction is maintained by morphology and the thickness of the oxide film. [7].Usually, the color of the oxide produced in the process of anodic oxidation is a measure of the thickness of the film. This relation between color and thickness depends upon on the anodization process as well as the electrolyte [8]. A slight modification in these parameters enables the modifications of the coloration of the titanium oxide surface.

1.2 OBJECTIVES

The present work is aimed to study the surface morphology, hardness and wettability properties of titanium oxide layer deposited on Ti-6Al-4V surface through the method of anodic oxidation. The objectives to be followed during the course of this entire work are as follows:

1. Anodic Oxidation of Ti-6Al-4V.

2. Preparation of working electrolytes

3. Process parameter study of anodic oxidation technique.

4. Characterization Techniques

- ⇨ Microstructure and morphology (SEM)
- ⇨ Chemical analysis and phase identification (XRD)
- ⇨ Micro-Hardness Analysis (Vickers's Hardness Test)
- ⇨ Wettability studies

5. Biomedical applications and future scope.

1.3 SCOPE OF THE PROJECT

The organization of the rest of the thesis is as follows. The concept of anodic oxidation, its basic mechanism, applications, parameters for improving deposition, surface morphology changes with parameters and brief review of literatures are provided in chapter 2. A detailed experimental study and different characterization techniques used and studied are provided in chapter 3. In chapter 4, methods, solution preparation and a basic scheme of work have been presented. A summary of the main results along with conclusions is presented in chapter 5. References used to summarize the entire project work have been provided at the end.

CHAPTER 2

LITERATURE SURVEY

2.1. BIOMATERIALS

Biomaterial is a substance that interacts with biological systems. The development of biomaterials, as a separate branch of science, is relatively fifty years old. According to the view held in 1980's (Passive and inert point of view) a biomaterial was to be classified as any substance or a drug, of synthetic or natural origin, which can be used for any usage alone or as part of a discrete system and that enhances any tissue, organ or function of the body. The modern view however, states that a biomaterial is such a material that can be used profusely used in a medical device and can also be designed to interact with biological systems. Research on biomaterials surface has become one of the current topics in biomaterials and biomedical engineering. [9]. The word "biomaterial" is generally used to describe a wide variety of materials used for biomedical applications. Controversies still arise on where exactly the margin lies between a genuine biomaterial and a biomedical device. As a matter of fact, many materials that are utilized as parts of a complicated replacement, for instance, may or may not be regarded as a biomaterial, depending on the working definition of the word [10].

There are some distinct advantages of using a biomaterial for biological purposes. Firstly, a biomaterial must be biocompatible; i.e.it should not produce an adverse response inside the body. Additionally, it should also be nontoxic and non-carcinogenic. Furthermore, the biomaterial should also possess appropriate physical and mechanical properties to serve as an enhancement or replacement of body tissues. For everyday usage, a biomaterial should be convenient to being formed in versatile shapes, have a low cost, and should be readily available [11].On the other hand, there are several distinct disadvantages attached with biomaterials such as poor tissue integration, no growth or adaptation, adverse reaction with surrounding tissue, loss of mechanical integrity with time, increased risk of infection and finally lack of biologically relevant instructive properties [12]. With improved and better medical facilities worldwide, increasing population nowadays is living to advancements in today's world. As a result, the chances of body parts such as those subjected to stress and pressure regularly like bones and joints, wearing out and becoming completely redundant are much greater over an extended period of time. Thus, implants are being increasingly used now days to replace the functioning of bones and joints. Since these parts are subjected to various stresses, the strength of these implants is crucial to absorb all of the stress that could be inflicted upon them. Properties such as

good mechanical properties, high corrosion resistance, cheap, a good fatigue life, and no wear and tear are highly desirable while the active functioning of the implant.

2.2. TYPES OF BIOMATERIALS

According to general classification, biomaterials can be usually divided in the following categories:

2.2.1. METALS

Metals are most commonly used for load-bearing implants. Some common orthopaedic surgeries involve the implantation of metallic implants. The body implants range from simple wires and screws to fracture fixation plates and total joint prostheses for hips, knees, shoulders, ankles, and so on. Metallic implants are nowadays increasingly used in maxillofacial surgery, cardiovascular surgery, and as dental materials. Out of those many metals and alloys which are used for medical device applications, the most commonly employed are stainless steels, commercially pure titanium and titanium alloys, and cobalt-based alloys. A wide variety of materials are generally used for medical purposes. These include but are generally not restricted to ceramic, glasses, metallic and polymeric biomaterials. Among these materials, metallic biomaterials find usage where load bearing structures are required such as in orthopaedics and dentistry. The advantages of using metallic biomaterials include the relatively easy fabrication methods of both simple and complex shapes by the help of well-established fabrication techniques such as casting, forging, machining. The high strength, low weight ratio and outstanding corrosion resistance inherent to titanium and its alloys has led to a wide and diversified range of successful applications which need high levels of reliable performance in surgery and medicine as well as in aerospace, automotive, chemical plants, power generation grids, oil and gas extraction, sports and major industries. In majority of these and other engineering applications titanium replaces heavier, less serviceable and less cost effective materials. Designing with titanium has resulted in reliable, economic and more durable systems and components, which have substantially exceeded performance and service life expectations. Titanium is available in several different grades.

2.2.2. POLYMERS

A huge plethora of polymers are used in medicine as biomaterials. They have widespread applications ranging from facial prostheses to tracheal tubes, from kidney and liver parts to heart components, and from dentures to hip and knee joints [13]. Accurate mixtures of synthetic and natural polymers can form a new class of materials with enhanced mechanical properties and biocompatibility as compared to those of single components. They have been termed as bioartificial or biosynthetic polymeric materials [14].Natural polymers are usually biocompatible, whereas synthetic polymers can contain a residue of initiators and other compounds or impurities that inhibit cell growth [15]. Synthetic polymers have commendable mechanical properties and thermal stability, and are much better than several naturally occurring polymers [16]. There is, however a limitation in the performance of several natural polymers in comparison to synthetic polymers. Synthetic polymers can be processed into a wide range of shapes, whereas for natural polymers several shapes are not easily obtained; for example, processing at an elevated temperature can destroy their native structure [17].Nascent polymeric materials based on the blends of natural polymers should be biocompatible and should also possess good thermal and mechanical properties for use in biomedical applications [18].

2.2.3. CERAMICS

Over the time, ceramics have seen increasing uses as restorative materials in dentistry including materials for crowns, cements and dentures However; their use in other biomedical fields has not been as exhaustive, compared to metals and polymers. For example, the relatively poor fracture toughness of ceramics severely inhibits their use for load-bearing applications.

2.2.4. COMPOSITES

Carbon-carbon and carbon reinforced polymer composites are of great importance in the field of bone repair and joint replacements due to their low elastic modulus levels. Unfortunately, these materials have not showed a desirable combination of mechanical and biological properties appropriate to these applications. Composite materials are frequently used extensively for prosthetic limbs, where their combination of low weight and high strength make them ideally suited for such applications.

2.2.5. NATURAL BIOMATERIALS

One of the many advantages of using natural materials for implants is that they bear resemblance to the materials present inside the body. The usage of bio materials is growing healthily in this regard. There are certain areas where these polymers excel as compared to the synthetic materials. Firstly, natural materials do not offer the problems of toxicity, which is often faced by synthetic materials. Next, they carry specific protein binding sites and other biochemical signals that assist in tissue healing or integration. On the contrary, natural materials can be subject to problems of immunogenicity. Another problem faced by natural polymers is their tendency to denature or decompose at temperatures below their melting points. This drastically limits their fabrication into implants of different sizes and shapes.

2.3. TITANIUM AND ALLOYS AS BIOMATERIALS

Various metallic materials have been used for total hip replacements as well as other joint replacement surgeries, i.e., knees and shoulders. Some other potential applications include spinal fixation devices, cardiovascular stents, and, most recent are the replacement spinal discs. The material list includes stainless steel, Co–Cr–Mo alloys, titanium alloys and other more specialized alloys, e.g., Au–Pd. Of these titanium alloys, the subject of the present report, offer several advantages, including lower elastic modulus, excellent corrosion resistance and enhanced biocompatibility [19].

Ti-6Al-4V is the most widely used of all titanium alloys since it can be heat-treated to various levels and is comparatively easy to be machined[20]. The attainment of long-lasting metal-metal bonds utilizing titanium adherends has been an important area of concern, particularly for aerospace and defense industries. Therefore based on this concern, most research into the effects of the surface-treatment of the adherend has been carried out by these specific industries.

Titanium and titanium-based alloys are commonly used biomaterials for transcutaneous implants because of their mechanical strength, biocompatibility, non-toxicity, corrosion resistance and ease of processability [21, 22].These materials are used in a large range of clinical devices such as prostheses, craniofacial and dental implants. When an implant is placed in a physiological environment, metal ions are released which could cause local and systemic effects. In the case of the Ti-6Al-4V alloys, titanium ions may accumulate in local tissues after long periods of time [23] giving rise to dark tissue staining with unknown consequences [24]. Aluminum is a

transportable element, which is capable of reaching out to the distant parts of the body [25] and influences some forms of bone disease and neurological disorders [26]. Vanadium is also considered to be an essential element in the body, but may have toxic consequences, if produced at an excessive level. Vanadium can also act as a body irritant, if excess amount of vanadium is produced [27].

An increased rate of implant osseointegration is influenced by various factors such as the tissue adequacy of implant material, design formation, surface conditions, surgical region condition, surgical tools and techniques, and finally implants loading methods [28]. The surface condition is known to be the most crucial factor affecting implant osseointegration [29, 30]. Titanium is used as a medical and dental material for commendable mechanical features, anti-corrosion properties, and bioaffinity [31]. Since the chemical combination of the metal with bone is known to decrease the active induction of bone formation, however, the healing period is extended [32]. Studies on surface treatments of titanium are in progress to increase the adhesion of bone tissue and implants. It is clear that any reduction in ion release will prove to be beneficial for the patient and may increase implant lifetime, thereby avoiding the need for re-surgery. This is mostly true for a porous and cementless implant wherein a large surface area of the implant is exposed to the bioenvironment.Ti-6Al-4V is an inert implant material with excellent mechanical properties. The corrosion resistance is mainly due to the formation of a stable passive film which rapidly forms on the alloy and provides a barrier between the bio environment and alloy substrate. Previous works have reported that modification of the surface oxide may reduce the metal ion dissolution into saline solution. The present work analyses this effect further in a hope that simple and low cost treatments put into regular practice may be able to decrease metal ion release from the metallic implants.

2.4. TECHNIQUES OF SYNTHESIS OF TiO_2 LAYER

2.4.1. TEMPLATE-ASSISTED SOL-GEL METHOD

A general method for the synthesis of TiO_2 layer is template-assisted sol–gel synthesis. The system of template-directed oxide synthesis makes the use of the positive templates and negative templates. With the use of positive templates such as CNT’s, the inner diameters and the length of the resulting nanotubes are respectively decided by the length of the diameters and the original 1-D templates. With the use of negative templates, porous membranes offer excellent size

uniformity in the morphology of the formed oxide on a nanometer scale. In addition to the mono dispersity of the oxide formed, this method can also produce a thin and as well as a controllable wall layer of titanium oxide, which would allow for better applications [33].

2.4.2 HYDROTHERMAL TREATMENT

The hydrothermal route to manufacture titanium oxide is mainly used to prepare tubular shaped nanotubes. Under alkaline hydrothermal conditions, the formation of titanium nanotubes occurs immediately and is characterized by a huge distribution of morphological parameters. [34]. Hydrothermal technique is one of the most commonly used and effective techniques for the processing of a great variety of materials. Hydrothermal synthesis is a very promising method to obtain nanostructures where polymorphism, particle size crystallinity and morphology could be easily controlled as required compared to any other technique because of highly controlled diffusion in the crystallization medium [35]. As a low temperature technology, hydrothermal synthesis is environmentally friendly as the entire reaction takes place in aqueous solutions within a closed system, using water as the reaction medium. TiO_2 nanotubes are obtained when TiO_2 powders are mixed with sodium hydroxide aqueous solution maintained at room temperature for 20 h in the autoclave [36].

2.4.3 ANODIC OXIDATION

In this context, TiO_2 layer fabricated by anodic oxidation has received considerable attention for its superior semiconducting and photo electrochemical properties, in addition to their high surface-to-volume ratios provided by the additional area enclosed inside the hollow structure. The anodic formation TiO_2 layer in various electrolytes and with different conditions has undergone stringent investigation to further improve the structure and control the dimensions of the oxide layer [37]. Among the reported techniques, electrochemical anodization of titanium is a relatively convenient route to fabricate highly uniform titanium dioxide layer. Typically, electrolyte composition and applied potential are the most important anodization variables for the formation of TiO_2 layer besides temperature [38].

2.5. ANODIC OXIDATION

2.5.1. MECHANISM OF ANODIC OXIDATION

The titanium alloy implant spontaneously passivates to create an adherent titanium oxide surface

film. This film is initially less ordered and this results in higher titanium ion mobility. A boundary layer model has been representing the oxide-solution proposed to interface [39, 40].and three main regions in the solution have been proposed:

1. The surface boundary layer, where structured water molecules are physiorbed to the hydroxylated surface by hydrogen bonding.
2. The surface charge layer, where positively charged species such as hydrated inorganic ions adsorb onto the surface.
3. The bulk electrolyte layer, which is far enough away such that no species are directly taking Part in the dissolution process.

It is generally observed for all the processes that in the first few seconds of the anodization, the resistance thereby reducing the current densities. In the second phase, the current intensity starts to increase due to the solubility of the Ti oxide in acidic HF-containing solutions and the oxide layers begin to grow randomly. This is further supported by a more stable and regular competition between the self-aligned titanium oxide growth and therefore, the current slowly decreases. The current intensities represent regular periodical fluctuations which are related to the solution and dissolutions of the oxide films. These strong current oscillations can be ascribed to a passivation and depassivation reaction related to the TiO_2 oxide formation and oxide dissolution that are competing with each other during the self-aligned titania oxide layer formation [41].

In this work, an anodic oxidation method has been used to fabricate TiO_2 on the surface of Ti-6Al-4V [42, 43]. This method is in use due to its several distinct advantages. Firstly, it allows us to select the desirable composition of electrolytes used for doping; since this is advantageous for controlling the band gap structure of the oxide layer formed [44,45]. Secondly, anodic oxidation occurs in equilibrium due to the thermodynamic reaction [46] and provides proper adhesion and interfacial strength [47], which enables the growth of stable oxide layers. Thirdly, a porous microstructure is formed due to the competitive reaction between oxide formation and chemical dissolution [48, 49], and distinct structures with tubular pores could be obtained on further application of the voltage [50]. Finally, the process fundamentals have been established for coloring titanium and its alloys [51], which is advantageous for application convenience. The conversion potential in anodic oxidation changes the microstructure and phase of the oxide. A subsequent rise in the conversion potential promotes crystallization, and therefore increases the

oxide thickness. Further increase in the potential leads to some sparking due to electric arcs through dielectric breakdown and a porous structure appears [52]. Other electrochemical parameters such as anodization time, applied current and the electrolyte concentration could affect the crystal structure and microstructure of the oxide. [53, 54].

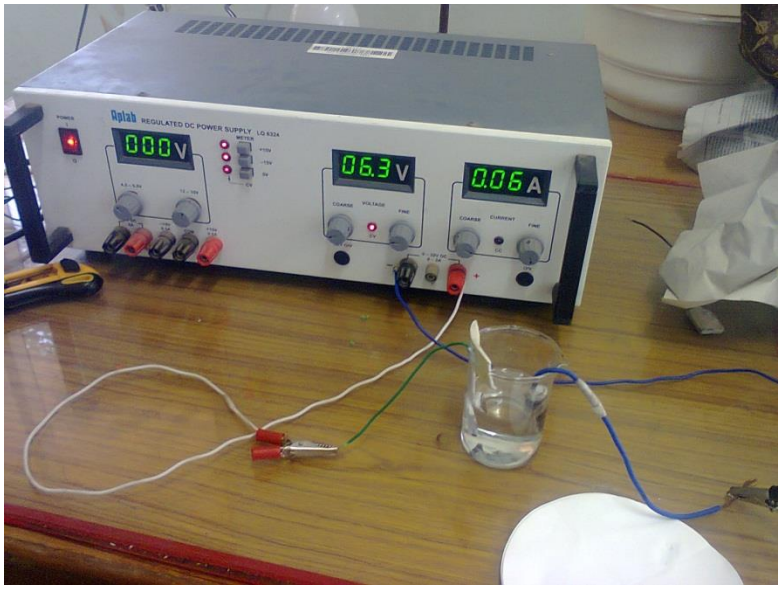


Fig.1: Apparatus for anodic oxidation method

2.5.2. EFFECT OF PROCESSING PARAMETERS

The parameters related to the anodic oxidation are mostly process related parameters. The process related parameters are deposition time, applied voltage, concentration of the working electrolyte.

2.5.2.1. EFFECT OF DEPOSITION TIME

It has been observed that during the process of anodic oxidation, when the deposition time increases the rate at which the oxide film is formed also increases.

2.5.2.2. EFFECT OF APPLIED VOLTAGE

It is observed that the amount of deposition increases with the increase in voltage. When anodic oxidation was carried out in the range of 10-20V, the deposit layer so formed is generally non-uniform in nature and did not cover the entire surface of the sample substrate. On the other hand, at a constant voltage of 30V, a more-uniform deposit is likely to be obtained.

2.5.2.3. EFFECT OF CONCENTRATIONS OF THE WORKING ELECTROLYTE

The concentrations of the working electrolyte are also known to affect the layer of deposit so formed. In fluoride-containing electrolytes, the anodization of Ti-6Al-4V is accompanied with the chemical dissolution of Ti oxide due to the formation of Ti^{2-}_{6}. This dynamic oxide formation/dissolution equilibrium is established during large periods of the anodization process controlling the time width of the porosity developed; self-ordering effects and the thickness of the oxide layer. One of the causes of implant failure results from the lack of initial bonding between the implant surface and bone. Accordingly, methods for improving the bioactive bone-bonding ability of an implant by modifying the material surface have been examined [55, 56].

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. MATERIALS REQUIRED

Square pieces of Ti-6Al-4V are used as anode material [57]. A pure graphite rod acted as the cathode. Acetone, ethanol(absolute) and Magnesium Sulphate, and Magnesium Chloride, Sodium chloride and D-glucose, Sodium hydrogen carbonate while Di-sodium hydrogen Phosphate are used to prepare Hank's solution. Hydrofluoric acid (48%), Glacial Acetic acid and hydrogen fluoride are used for making electrolytes. All the solutions and the glassware were autoclaved prior to being used and the desired reagents were prepared in de-ionised water.

3.2. SAMPLE PREPARATION FOR ANODIC OXIDATION

3.2.1. CUTTING

Ti-6Al-4V samples were cut from a titanium sheet in the dimension of 12mm×10mm×5mm using a hex blade.

3.2.2. GRINDING

Grinding of crude and rough samples was done on a belt grinder. Grinding was done to produce smooth edges.

3.2.3. PAPER POLISHING

Paper polishing was done using four types of emery paper graded as 1/0, 2/0, and 3/0. These papers have abrasive particles on their surface. 1/0 has more roughness then the other two papers. The roughness of the paper decreases from 1/0 to 3/0. Effective polishing was achieved by using two consecutive emery papers in the perpendicular fashion on the Ti-6Al-4V samples. Paper polishing was done to remove roughness of the material received.

3.2.4. CLOTH POLISHING

The next step after paper polishing was Cloth polishing. Cloth polishing was done on a velvet pad on a cloth polishing wheel. Also known as buffing; this was used as a pre-requisite for finishing the polishing process. Alumina paste was used as a polishing material in the cloth polishing .This cloth polishing was done to remove minor scratches that remained after paper polishing.

3.2.5. DIAMOND POLISHING

Diamond polishing was the last step after cloth polishing. Diamond polishing was done only for

removing very fine scratches that remained after cloth polishing. In, this procedure, diamond paste was used along with Hi-Fin spray. Finally, a mirror-like surface was produced after diamond polishing was done.

3.3. SOLUTION PREPARATION FOR ANODIC OXIDATION

3.3.1. PREPARATION OF CH_3COOH and 0.5 M HF SOLUTION

The first electrolyte used for the anodic oxidation of titanium sample was CH_3COOH and 0.5M HF solution. To prepare a 100 ml solution, 0.86ml of 0.5M HF was taken according to relevant empirical calculations and was stored in a volumetric flask. Finally the volume was made up by adding acetic acid slowly into the flask. The solution was then stored for further use.

3.3.2. PREPARATION OF 1M H_2SO_4 and 0.15% HF SOLUTION

The second electrolyte used for the anodic oxidation of titanium sample was 1M H_2SO_4 and 0.15 %HF solution. To prepare a 100 ml solution, 0.27ml of 0.15%HF was taken according to relevant empirical calculations and was stored in a volumetric flask. To prepare a 1M H_2SO_4 solution, 5.56 ml of sulphuric acid was taken. Finally the volume was made up by adding de-ionised water slowly into the flask. The solution was then stored for further use.

3.3.3. PREPARATION OF 1.5%HF SOLUTION

The third electrolyte used for the anodic oxidation of titanium sample was 1.5wt% HF solution. 7.2 ml of 48% hydrofluoric acid was taken according to empirical calculations and kept in a volumetric flask. Finally the volume was made up to 100 ml by slowly adding de-ionised water into the volumetric flask. The solution was then stored for further use.

3.3.4 PREPARATION OF HANK'S SOLUTION

1L of Hank's solution was prepared using 0.185g of $CaCl_2$,0.4g of KCl, 0.06g of KH_2PO_4 , 0.1g of $MgCl_2.6H_20$, 0.1g of $MgSO_4.7H_2O$, 8g of NaCl, 0.35g of $NaHCO_3$, 0.48g of Na_2HPO_4 and 1.0g of D-glucose. All the components were weighed using a digital weighing balance. The final volume was made up by de-ionised water. Hank's solution was prepared for determining the wettability of the TiO_2 oxide surface deposited onto the sample surface.

3.4. EXPERIMENTAL PROCEDURE FOR ANODIC OXIDATION

The experimental set-up for anodic oxidation used in this work is a 2-electrode system. The oxidation was carried out using a graphite rod as the cathode and the titanium samples as anode respectively. The temperature of the experimental set-up was maintained at a constant room temperature. [58].In this work, TiO_2 layer deposition on titanium substrates was achieved by carrying out the anodic oxidation at a constant voltage [59]. A DC supply was provided by APLAB regulated DC power supply.

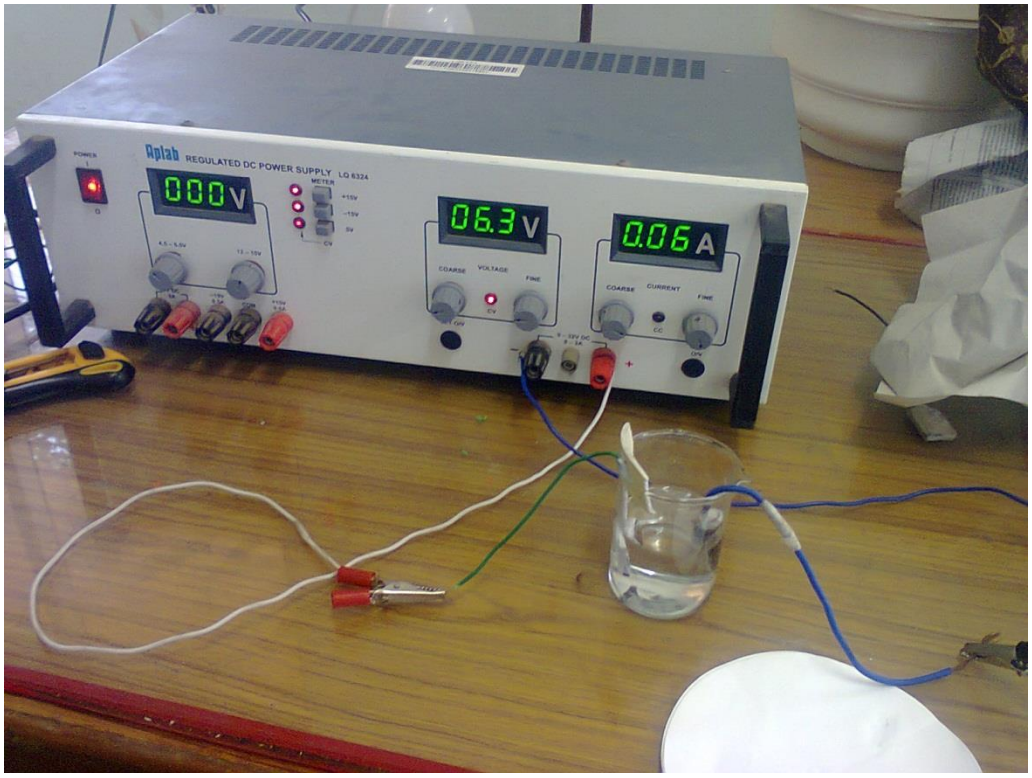


Fig.2: Working Set-up for Anodic Oxidation

3.5. CHARACTERIZATION TECHNIQUES

3.5.1. MICROSTRUCTURE EVALUATION

3.5.1.1. SCANNING ELECTRON MICROSCOPIC (SEM) STUDIES

The scanning electron microscope (SEM) analyses the surface morphology ofTi-6Al-4V. It is an electron microscope and captures the images of the sample surface by scanning it with a high-energy beam of electrons. The SEM is able to produce very high-resolution images of a surface, showing details smaller than 1 nm in size. SEM also produces images of high resolution, which

means that closely spaced features can be examined at an ultra-high magnification .The beam of electrons interacts with the atoms that constitute the sample producing signals that contain information about sample surface topography, composition as well as electrical conductivity.

SEM characterization of the oxide layers was performed using JEOL JSM-5300 microscope (acceleration voltage 15 kV). The oxide samples were placed in the SEM‟s sample holder using graphite impregnated adhesive conductive black "carbon tape". This sample holder was then ushered inside the instrument. Finally, these samples were visualized under SEM at various magnifications e.g. 1500X, 2500X, 5000X, and 7500X.

Fig. 3: JEOL JSM-6480LV Scanning Electron Microscope

3.5.2. X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) is a versatile that reveals detailed information about the composition and crystallographic structure of natural and manufactured substances. The powder diffraction method is generally used for characterization and identification of polycrystalline phases. The analysis is based on the principle of constructive interference i.e. when a monochromatic X-ray beam with wavelength lambda (λ) gets projected onto any crystalline substance at an angle theta (θ), diffraction takes place when the distance travelled by the X-rays reflected from two consecutive planes differs by a number n of wavelengths. When X-rays get scattered from a crystal lattice, various peaks of scattered intensity are observed, which simultaneously correspond to the following two conditions:

1. The angle of incidence should be equal to the angle of scattering.
2. The path-length difference is equal to an integer number of wavelengths.

In XRD analysis, a graph is plotted between 2θ and counts .In XRD analysis the Bragg's

equation is followed,

$$n\lambda = 2dSin\theta$$

Where,

n is the number of wavelengths,

λ is the wavelength,

d is spacing between the planes in the atomic lattice,

θ is the angle between the incident ray and the scattering planes

The X-ray diffraction patterns of the samples were recorded on a Philips Analytical ltd, Holland (PW3040) using Ni-filtered Cu-Kα radiation. The range for XRD characterization was selected as 20-80 degree with a scan speed of 2 degrees per minute using Bragg- Brantano configuration. After deposition, the oxide layer so obtained was examined by X-ray diffraction (XRD) to examine the phases formed in the oxide layer. Similar study was also carried out on the on the as received Biomaterial. XRD was carried out in 2θ range of 20-80 and 2-3 degrees per minutes scan rate using Cu-Kα (α= .15406 nm) radiation in a Philips X'pert system.

Fig. 4: PANanalytical X-Ray Diffraction Equipment

3.5.3. MICRO-HARDNESS STUDIES

The hardness of the titanium oxide layer on the Ti-6Al-4V surface has been measured using LECO LM700 micro hardness tester which is shown in Figure 5. The machine has minimum 1gf and a maximum of 1000 gf load; Dwell time 5-99sec and Knoop or Vickers indenter is included. The test was carried out with 10 gf load for 15 seconds to ensure that the indentation is up to the

coating surface only. The hardness values were taken at 5 different places on the surfaces and average of these values were considered in this result.

Fig. 5: LECO LM700 Michro-hardness tester

3.5.4 WETTABILITY STUDIES

Wetting is the property of any liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together in close proximity. The degree of wetting or the wettability is determined by a force balance between adhesive and cohesive forces. Wetting is crucial in the bonding or adherence of two materials. Wetting and the surface forces that control wettability are equally responsible for other related effects, such as the so-called capillary effects. Irrespective of the amount of wetting, the shape of a liquid drop on a rigid surface is approximately a truncated sphere.

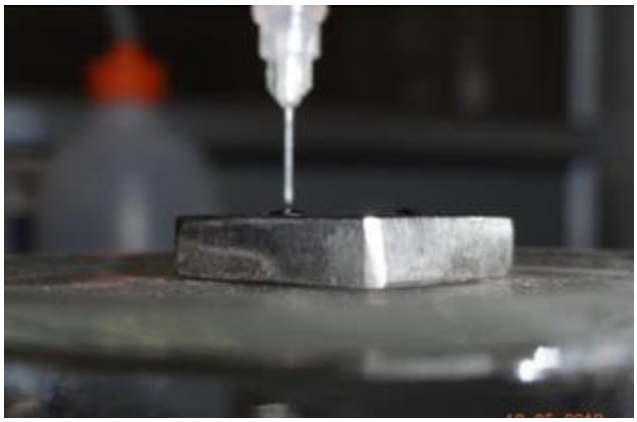
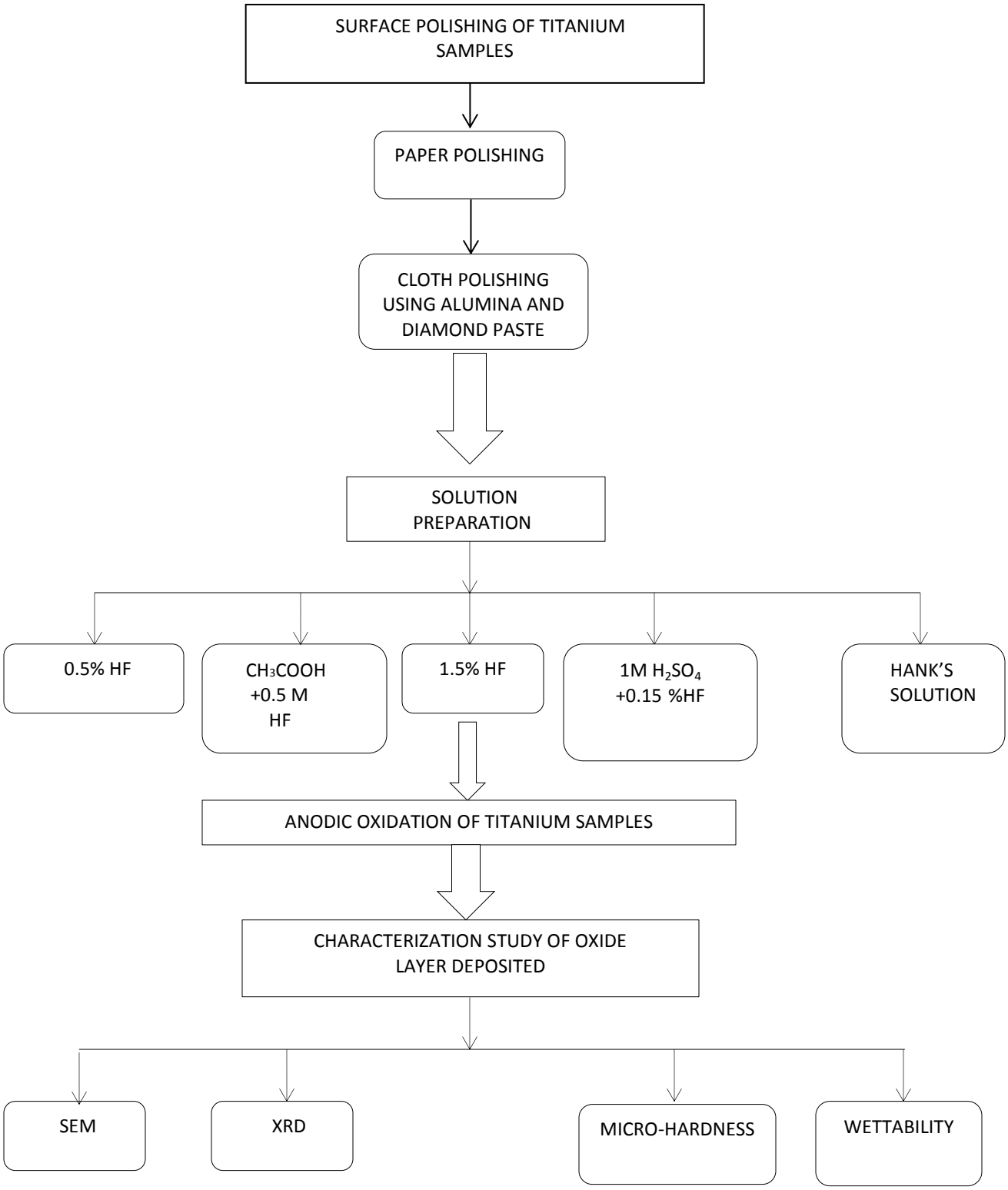


Fig. 6: Apparatus Design for Wettability study

3.6. BASIC SCHEME OF WORK



CHAPTER 4

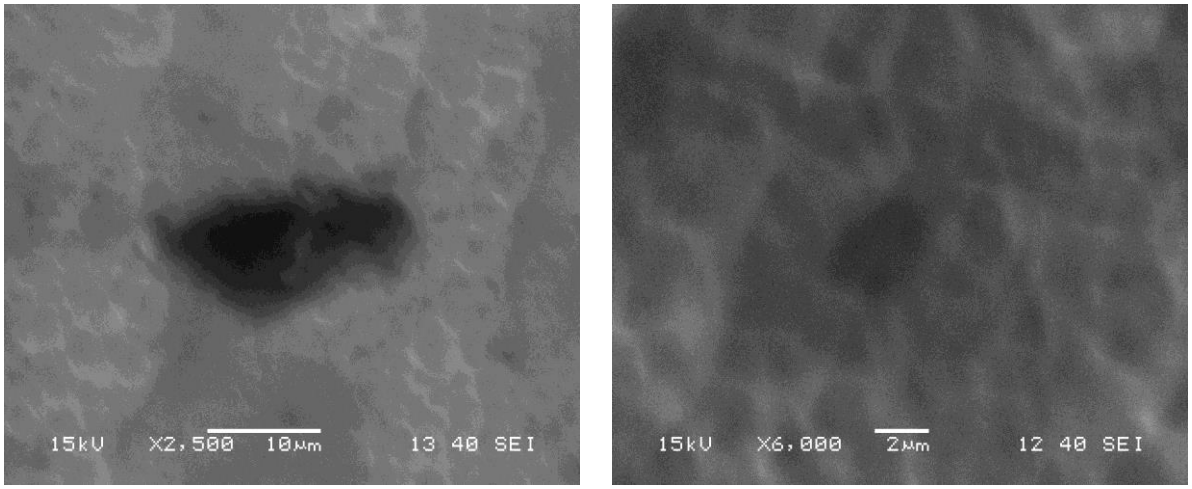
RESULTS AND DISCUSSION

4.1. MORPHOLOGICAL CHARACTERIZATION

It has been observed that in anodic oxidation, the morphological nature of the oxide grown on the surface depends on real-time parameters such as the operating voltage, reaction time, and current density. In this work, the nature of the working electrolyte and the reaction time have used as the varying parameters.Ti-6Al-4V surface has been polished and anodically oxidized in different solutions. The detailed study of oxide surface is discussed under this section.

4.1.1. SCANNING ELECTRON MICROSCOPY (SEM)

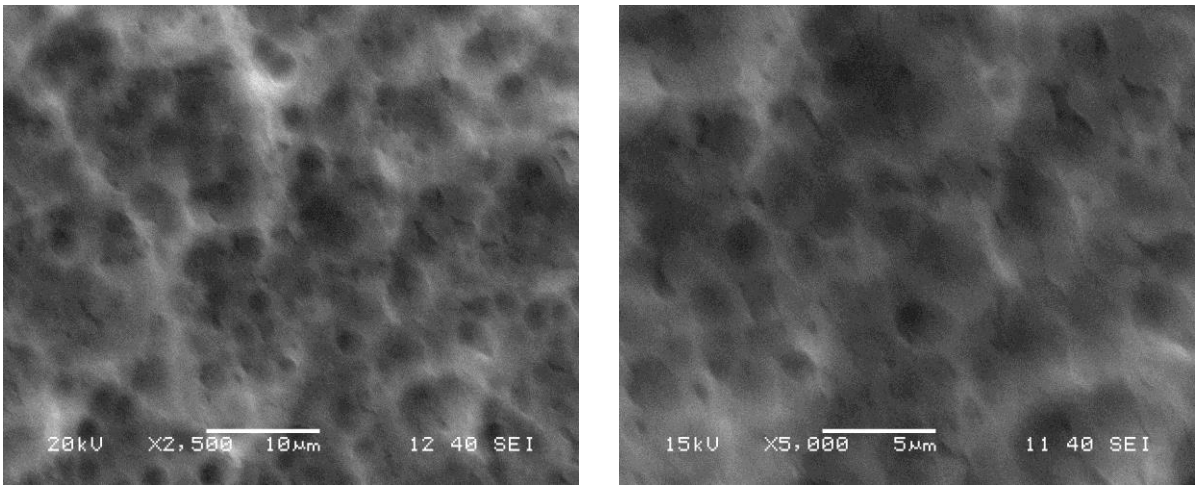
Figure 7.1 shows scanning electron micrograph of the Ti-6Al-4V surface after anodic oxidation using CH_3COOH +0.5M HF as electrolyte .Ti-6Al-4V is treated anodically for three different time duration such as 4, 6 and 8 h. From the figure it has been observed that coating is continuous, uniform and crack free. The oxide layer is deposited throughout the surface in a globular form. At higher magnification numerous pores can be seen and the grain diameters are found to be 2 micrometer.



(a) **(b)**

Fig 7.1: SEM images of the Titanium oxide surfaces obtained on Ti-6Al-4V substrate with CH_3COOH+0.5M HF at different Magnification (a) at 1,500X and (b) at 6,000X for 4 H.

Figure 7.2 shows scanning electron micrograph of Ti-6Al-4V surface by anodic oxidation in CH_3COOH +0.5M HF for 6h. As the anodization time increase the structure of the oxide is more in the form of dimple shape this is because of the thickness of oxide layer increases and the ions consume at the bottom.



(a) **(b)**

Fig 7 .2: SEM images of the Titanium oxide surfaces obtained on Ti-6Al-4V substrate with CH_3COOH+0.5M HF at different Magnification for 6 H.

Figure 7.3 shows scanning electron micrograph of Ti-6Al-4V surface by anodic oxidation in CH_3COOH +0.5M HF for a period of 8h. Some micro-rough surface structures were observed randomly throughout the oxide surface, thereby indicating that the oxide deposition was not uniform and was rather distributed randomly over the sample surface. [62].As we increase the anodization time i.e. from 4 to 6 and to 8 h. (Fig. 7.3), a compact homogenous oxide is grown throughout the surface of Ti-6Al-4V.

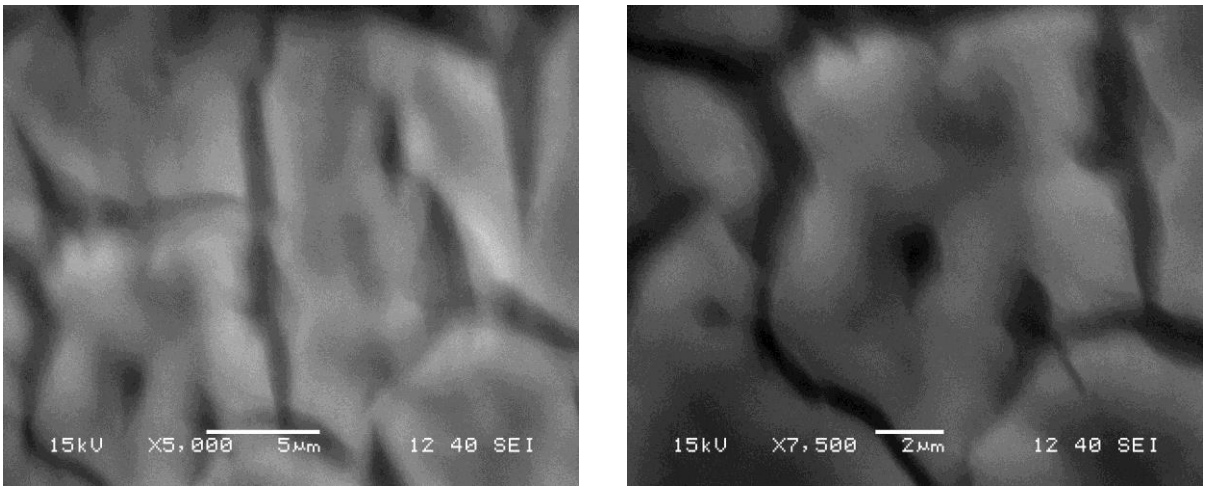
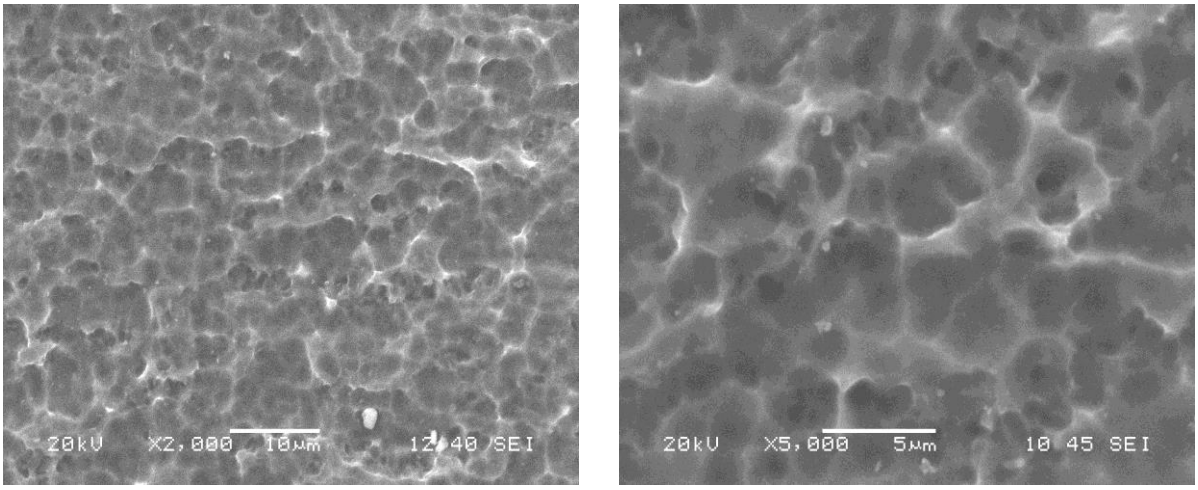


Fig 7.3: SEM images of the Titanium oxide surfaces obtained on T-i6Al-4V substrate with CH_3COOH+0.5M HF at different magnification for 8 H.

Figure 7.4 shows scanning electron micrograph of Ti-6Al-4V surface by anodic oxidation in 1M H_2SO_4 +0.15 % HF for a period of 4h. From the figure it has been observed that coating is

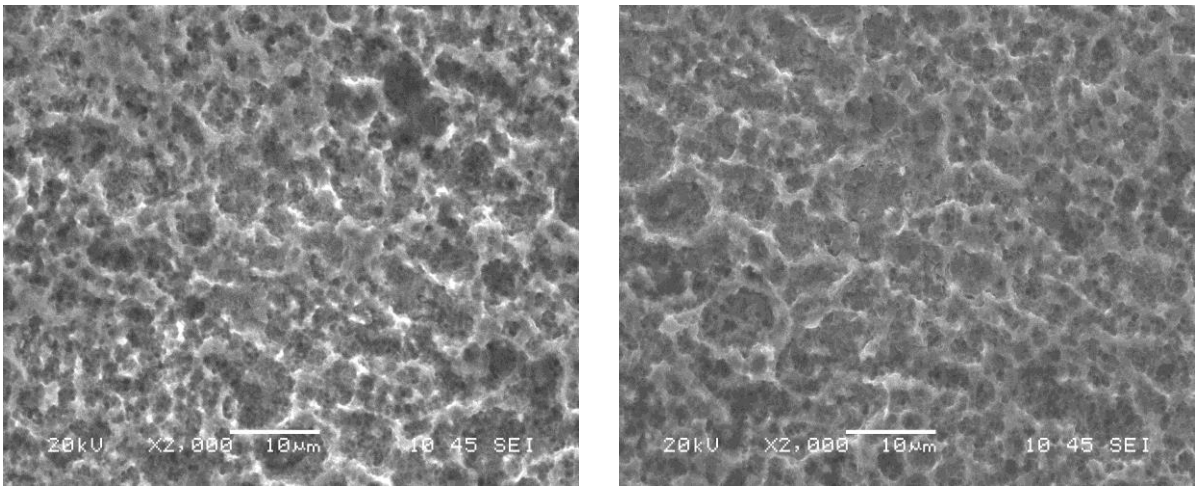
continuous, uniform and crack free. The oxide layer is deposited throughout the surface in a globular form. At higher magnification numerous pores can be seen and the grain diameter is found to be 5 micrometer.



(a) **(b)**

Fig 7.4: SEM images of the Titanium oxide surfaces obtained on Ti-6A-l4V substrate with 1M H_2SO_4+0.15 %M HF at different magnification for 4 h.

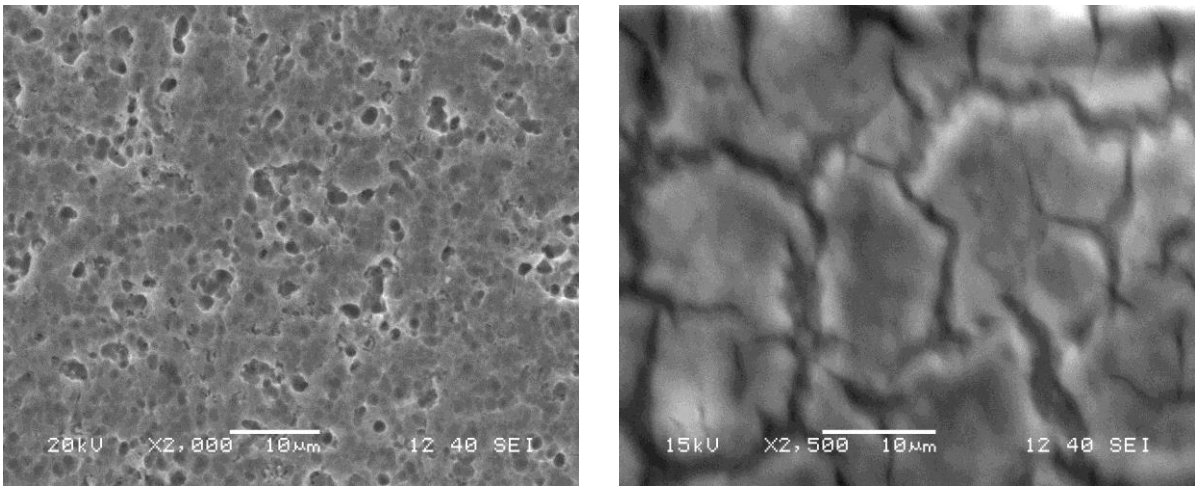
Figure 7.5 shows scanning electron micrograph of Ti-6Al-4V surface by anodic oxidation in 1M H_2SO_4 +0.15 % HF for a period of 6 H. the oxide layers are found to have agglomerated structures. It is evident from the figure that a porous oxide layer is grown uniformly covering almost the entire area of the sample



(a) **(b)**

Fig 7.5: SEM images of the Titanium oxide surfaces obtained on Ti-6Al-4V substrate with 1M H_2SO_4+0.15 %M HF at different magnification for 6 h.

Figure 7.6 shows scanning electron micrograph of Ti-6Al-4V surface by anodic oxidation in 1M H_2SO_4 +0.15 % HF for a period of 8h. The resulting SEM images shown are treated for 8 h. The oxide layers are found to have agglomerated structures, covering almost the entire area of the sample. Thus it is observed that for a time duration of 4h, an oxide layer was produced which had minor cracks. The cracks were consequently removed when the time duration was increased to 6 h. The oxide layer became denser and covered the entire sample surface when the time duration was further increased up to 8 h. this could be summarized in a way that the reaction time plays an important role in the deposition pattern. On the other hand, with the passage of time (Fig. 17.6, agglomerated structures are formed, covering almost the entire area of the sample [63].



(a) **(b)**

Fig 7.6: SEM images of the Titanium oxide surfaces obtained on Ti-6Al-4V substrate with 1M H_2SO_4+0.15 %M HF at different magnification for 8 h.

4.2 X-RAY DIFFRACTION (XRD) ANALYSIS

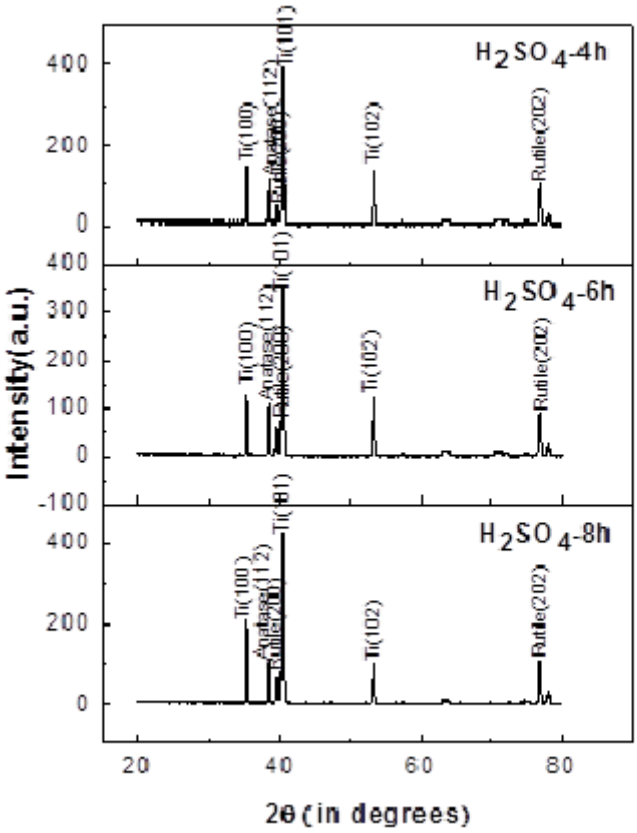


Fig 8: (a) XRD spectra of Ti-6A-l4V upon treated with H_2SO_4 on different time duration

Fig.8 (a) shows the XRD profile of the oxide layer on Ti-6Al-4V, treated with 1 M H_2SO_4+1.5%HF at various time durations. All the peaks for the anatase have been matched with JCPDS data base reference no. 84-1286, while the peaks for the α-Titanium have been matched with that of reference no. 44-1284. It can be seen that the patterns at 35 deg. And 48 deg. ascribed to the Ti (100) and Ti (101) crystal plane on the surface of the Ti-6Al-4V. The peaks correspond to the 38 deg. and 76 deg. confirms the presence of anatase and rutile phase respectively. It is clear from the graph that as we increase the time of reaction the intensities increases.

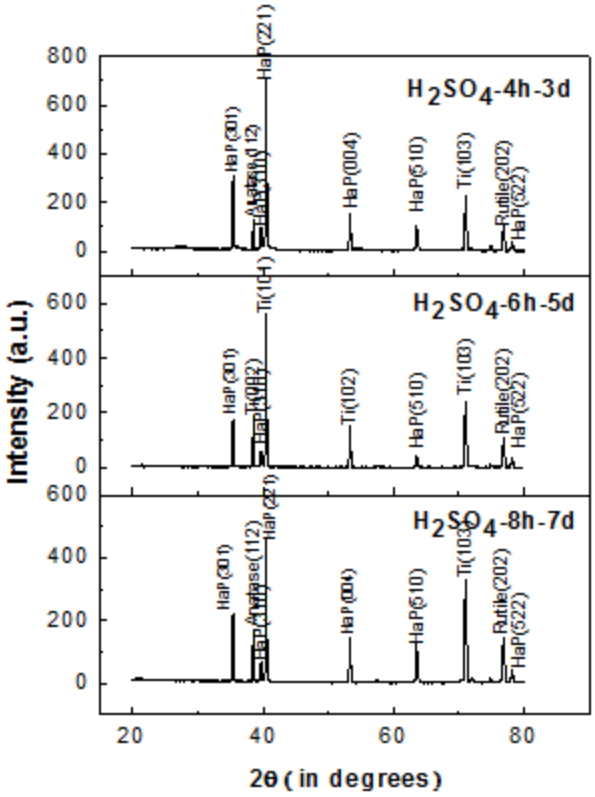


Fig.8 (b) XRD spectra of Ti-6Al-4V upon treated with $H_2SO_4$and HANK'S sol. on different time duration

Fig.8 (b) gives the XRD profile of the oxide layer on Ti-6Al-4V with 1 M H_2SO_4+1.5%HF and further with hank's solution at various time duration. All the peaks for the anatase have been matched with JCPDS data base reference no. 84-1286, while the peaks for the α-Titanium have been matched with that of reference no. 44-1284. The peaks correspond to the 38 deg. Confirms the presence of anatase phase while peak at 76 deg. confirms the rutile phase. Also, at different position, peaks corresponds to hydroxyapatite are found which confirms the deposition of calcium phosphate. This confirms that that a dense hydroxyapatite layer is formed on soaking to hank's solution after treating with the electrolyte. By comparing with fig.8 (a) it can be said that after soaking in hank's solution it has strong ability to form apatite in the crystal.

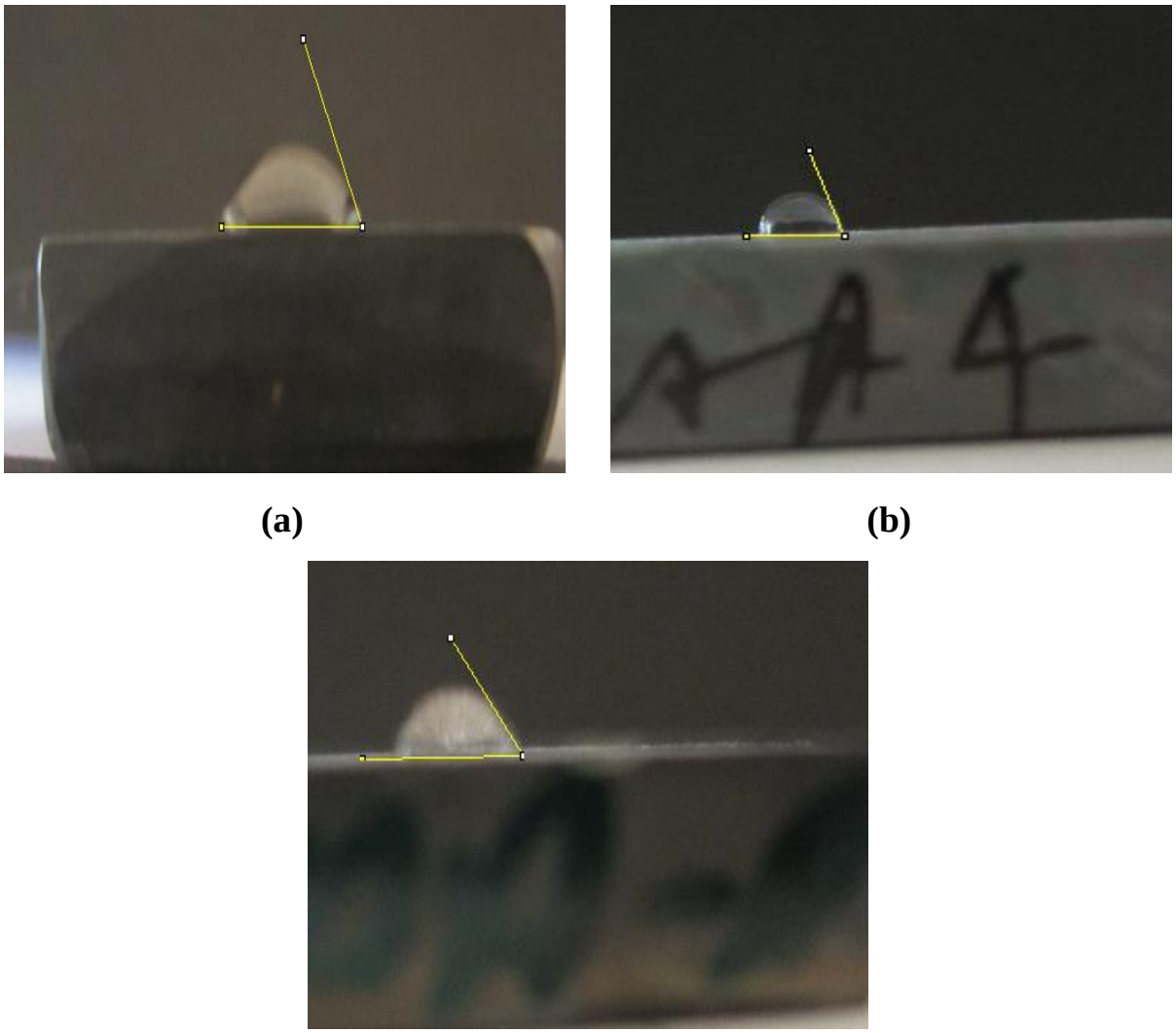
4.3 MICRO-HARDNESS ANALYSIS

Table 1: Vicker's Hardness No. for the untreated Ti-6Al-4V and anodically oxide Ti-6Al-4V is mentioned as a reference value.

Sample	Vicker's Hardness No. (VHN)
Bare titanium (as received)	330
CH_3COOH+0.5M HF (30 V, 4 h.)	263
CH_3COOH +0.5M HF (30 V, 8 h.)	396
1M H_2SO_4 +0.15 %M HF (30 V, 4 h.)	388
1M H_2SO_4+0.15 %M HF (30 V, 6 h.)	477
1M H_2SO_4+0.15 %M HF (30 V, 8 h.)	505

The micro-hardness of the oxide layer is measured by vicker's hardness tester by applying 100 gF. The values taken in the above table represent the average of the 5 values obtained for each sample. The increased in the hardness may be attributed to the formation of oxide layer over the surface. The table compares the different hardness values for the anodic oxidation reactions performed in different reaction time period .As can be inferred from the table, the VHN increases as the time period for the reaction increases. This suggests that with time, the depth of the oxide layer on the sample substrate increase and increase in hardness is attributed to the formation of more uniform oxide layer on the surface.

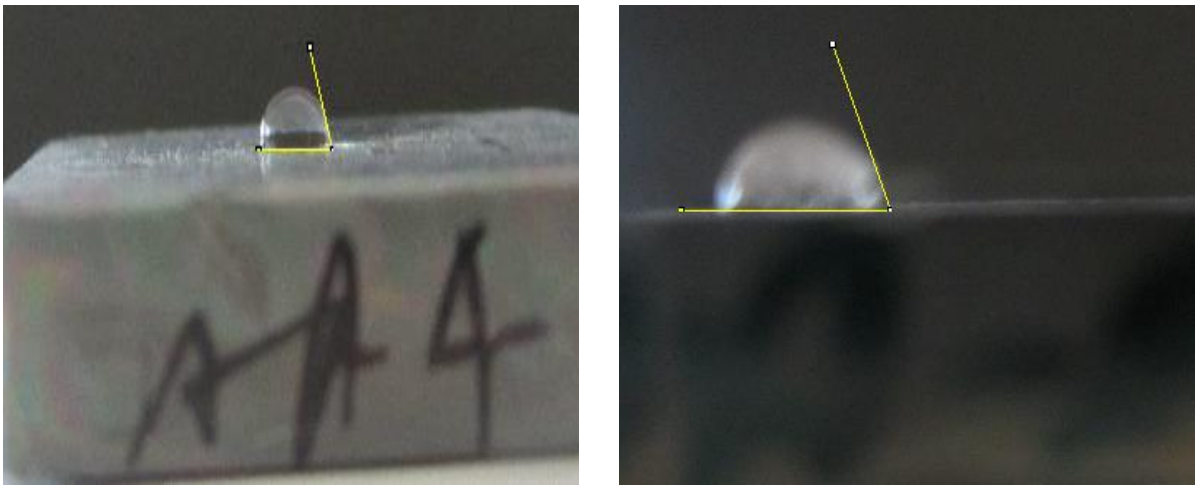
4.4 WETTABILITY ANALYSIS



(a) **(b)**

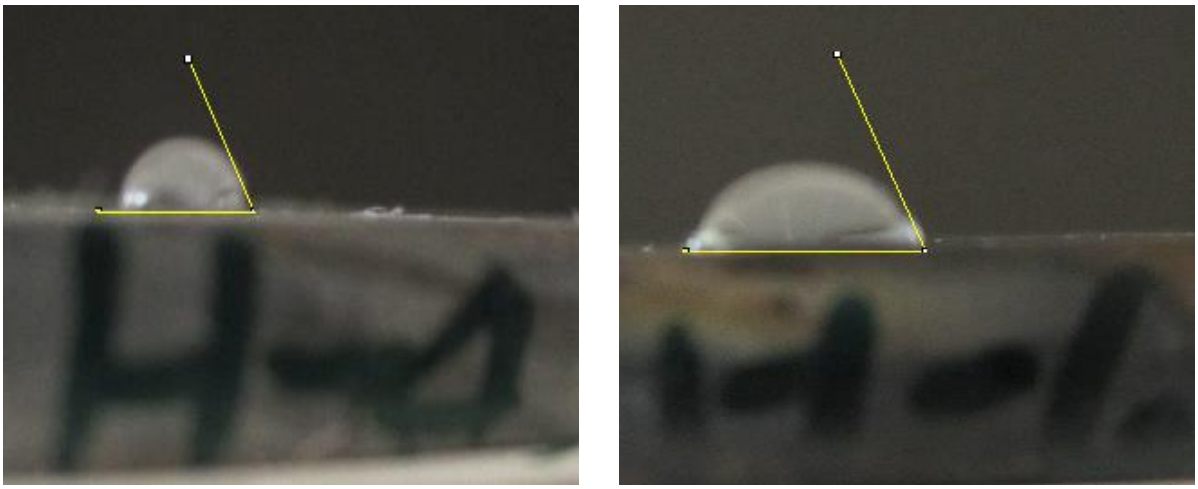
(c)

Fig. 10(A): Images of contact angle over (a) Bare Ti-6Al-4V,(b) oxide layer after treated with acetic acid (4 h) (c) Treated with acetic acid (8 h) at 30 V



(a) **(b)**

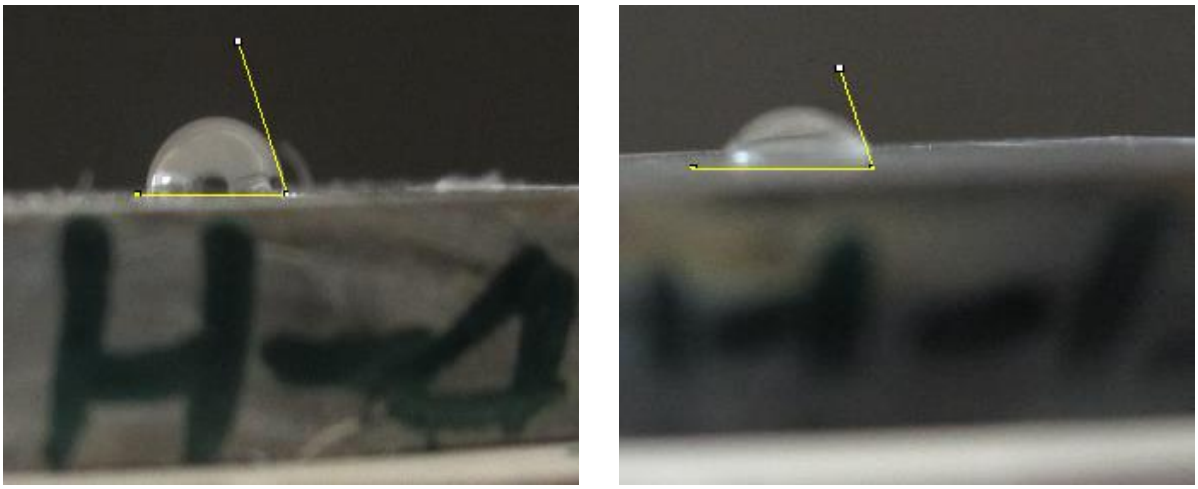
Fig 10 (B): Images of contact angle over (a) oxide layer after treated with acetic acid (4 h) (b) treated with acetic acid (8 h) at 20 V



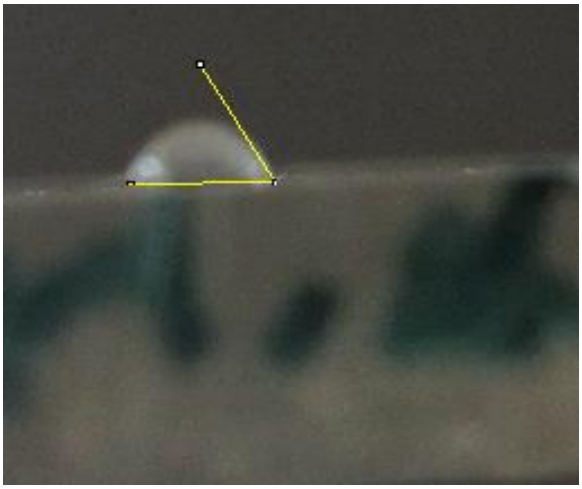
(a) **(b)**

(c)

Fig. 10 (c): Images of contact angle over Ti-6Al-4V treated with sulfuric acid (a) 4h (b) 6 h (c) 8 h at 30 V



(a) **(b)**



(c)

Fig. 10(d): Images of contact angle over Ti-6Al-4V treated with sulfuric acid (a) 4 h. (b) 6 h. (c) 8 h. at 20 V.

Table 2: Showing the contact angle (all in degree) obtained on treatment with the solution shown above with voltage 20 and 30 V respectively

Sample	Voltage	20 V	30 V
CH_3CHOOH + 0.5M HF (4 h.)		69	66
CH_3CHOOH + 0.5M HF (8 h.)		56	53
1 M H_2SO_4 + 0.15% HF (4 h.)		68	63
1 M H_2SO_4 + 0.15% HF (6 h.)		62	60
1 M H_2SO_4 + 0.15% HF (8 h.)		60	57
Bare Titanium-64 (As Received)		74	

Wettability analysis was carried out through measuring Contact angle by using Hank's solution onto the surface of the oxide layers. The wettability of the titanium dioxide films with different morphologies was investigated by Hank's solution contact angle (CA) measurement. For the as-prepared films, the CA exhibits a clear trend of decrease with the increase of anodizing voltages and time of treatment. (Fig. 10)When the anodizing voltage was 30 V, the samples became more wetted than 20V also with increase in time the samples show less contact angle. The CA on a polished Ti-6Al-4V sample is normally observed around 74deg [68]. Much higher CA are due to the increase of roughness. The CA of an oxidized sample at 20V was approximately 65deg. The drop spread up to 60deg. when a sample oxidized at 30V was used for the test. Therefore, it can be concluded that increase in voltage above 30 V improves the hydrophilicity of the surface due to the formation of highly polar O–Ti–O bonds. The titanium dioxide surfaces therefore exhibit low CA at voltages near 30V [69].

CHAPTER 5

CONCLUSIONS

CONCLUSIONS

1. Surface polishing was a crucial step in order to produce a mirror-like surface. This helped in a better oxide layer.

2. Uniform, continuous, adherent and crack-free TiO2 layer was obtained at 30 Volts and at longer time duration of 8 h.

3. Usually, titanium dioxide can exist in three crystalline forms, in which the anatase and rutile phases are more useful than the brookite phase. The crystalline form of the titanium dioxide prepared by electrochemical anodization under the specified condition was investigated by XRD, which confirmed the presence of anatase and rutile form of TiO_2.

4. The micro-hardness studies also confirmed the fact that the hardness of the sample oxidized for the maximum duration of time was the highest.

5. The wettability studies confirmed the hydrophilicity of the oxide surface at a voltage of 30V. This hydrophilicity is advantageous in terms of better cell growth and adhesion.

6. The wettability studies also confirmed the hydrophilicity of the oxide surface is more for longer time duration than shorter.

7. On soaking in Hank's solution after anodizing with sulfuric acid a dense apetite layers formed on the titanium surface.

8. Highly hydrophilic titanium dioxide coating is of great interest for various applications like biocompatible implants, anti-fog coating and self-cleaning surfaces.

9. As a further application of anodic oxidation of Ti-6Al-4V, a higher voltage condition can be provided so that nanotubular structures are formed with much ease and convenience. Titania nanotubes are of great significance in the field of biomedical science, drug delivery, photocatalytic activities and biosensor devices.

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